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New organotin(IV) complexes of nicotinamide, isonicotinamide and some of their novel phosphoric triamide derivatives: Syntheses, spectroscopic study and crystal structures

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ABSTRACT

Three novel phosphoramidate ligands with formula $RP(O)R'_2$, R = Nicotinamide(nia), R′ = $NHC(CH_3)_3$(**L_1**), $NH(C_6H_{11})$ (**L_2**); R = isonicotinamide(iso), $NH(C_6H_{11})$ (**L_3**) and their new organotin(IV) complexes with formula $SnCl_2(CH_3)_2(X)_2$, X = L_1 (**C_1**), L_2 (**C_2**), L_3 (**C_3**) plus $SnCl_2(CH_3)_2(L_4)_2$(**C_4**), **L_4** = $isoP(O)[NHC(CH_3)_3]_2$, were synthesized and characterized by ^1H, ^{13}C, ^{31}P,^{119}Sn NMR, IR, UV–Vis spectroscopy and elemental analysis. Two novel complexes of nia and iso with formula $SnCl_2(CH_3)_2(X)_2$, X = nia (**C_5**), iso (**C_6**) were also prepared and all the complexes were spectroscopically studied in comparison to their related ligands and to each other. The crystal structure of complexes **C_1**, **C_3**, **C_4**, and **C_5** were determined by X-ray crystallography. –Sn–Cl···H–N– major hydrogen bonds beside other electrostatic interactions produced a three dimensional polymeric cluster in the crystalline lattice of **C_1**, **C_3**, **C_5** and a two dimensional polymeric chain in **C_4**. Results showed that coordination of the phosphoramidate ligand (**L_4**) to Sn in **C_4** has been occurred from the nitrogen site of the pyridine ring similar to **C_5**, **C_6** in which there is no P═O donor site; however, in **C_1** and **C_3** the active donor site of corresponding ligands is P═O. It seems that in these complexes there is a competition between P═O and $N_{pyridine}$ donor sites and the influential factor which determines the winner site is the type of substituents on phosphorus atom.

1. Introduction

Nicotinamide (known also as vitamin PP, pellagra protective, vitamin B3, etc.) and isonicotinamide are two pyridine type ligands (see Fig. 1) with wide range of chemical and biological applications [1–3].

Nicotinamide is a part of the pyridine nucleotides as NADC and NADPC that plays a crucial role in biological oxidative chemistry and is essential for the human body [1,2]. Isonicotinamide possesses strong antitubercular, antipyretic, fibrinolytic and antibacterial properties. The mixed salts of this amide have extensive uses as drugs in various biological and medicinal processes [3]. Although numerous derivatives of nicotin- and isonicotinamide have been reported in the literature we could not find any phosphoramidate containing these amides. Phosphoramidates including –C(O)N(H)-P(O)– moiety have been used as O-donor ligands in the reaction with various metal ions up to now [4–15]. The presence of a peptide group in these compounds causes its diverse biological activity and used as anticancer drugs [16]. With respect to these important points about phosphoramidates, following to our previous works [17,18], we attempted to synthesize new phosphoramidates, including nicotinamide and isonicotinamide. In addition, since metal complexes of biologically important ligands are sometimes more effective than the free ligands [19] we also focused on complexation of nicotinamide, isonicotinamide and their new phosphoramidates (prepared in this work) with Sn metal. Although various complexes of these two amides (nia, iso) have been studied with several metals such as Mn, Co, Cu, Ni, Zn, Ag, Mg, Pb, Rh [20–25], to the best of our knowledge no organotin complexes of these types of ligands have been reported in literature. Organotin complexes have been studied by various methods in last four decades. Much of the interest in such complexes arises from their catalytic and biological activity [26] and their applications as fungicides or antifouling agents, antitumor and antimicrobial compounds [27–29].

In this work three novel phosphoramidate ligands with formula $RP(O)R'_2$, R = Nicotinamide(nia), R′ = $NHC(CH_3)_3$(**L_1**), $NH(C_6H_{11})$ (**L_2**), R = isonicotinamide(iso), $NH(C_6H_{11})$ (**L_3**); plus R = (iso), R′ = $NHC(CH_3)_3$ (**L_4**, reported in previous work [18]) were synthesized and spectrally studied in comparison to their new complexes with formula $SnCl_2(CH_3)_2(X)_2$, X = L_1 (**C_1**), L_2 (**C_2**), L_3 (**C_3**), L_4 (**C_4**). Furthermore two new organotin complexes with formula $SnCl_2(CH_3)_2(X)_2$, X = nia (**C_5**), iso (**C_6**) were prepared and the crystal structure of

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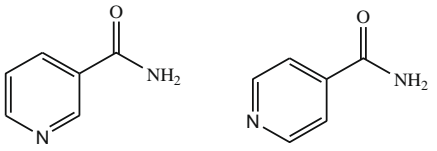


Nicotinamide(nia) Isonicotinamide(iso)

Fig. 1. Molecular view of nicotinamide and isonicotiamide.

complexes **C₁**, **C₃**, **C₄**, **C₅** were determined by X-ray crystallography. The characterization studies were carried out by ^{1}H, ^{13}C, ^{31}P, ^{119}Sn NMR, IR, UV spectroscopy and elemental analysis.

2. Materials and methods

2.1. X-ray measurements

X-ray data of compounds **C₁**, **C₄** were collected on a Bruker APEX-II CCD [56] and for compound **C₃**, **C₅** on a Bruker SMART 1000 CCD [57] area detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were refined with SHELXTL (for **C₁**, **C₃**, **C₅**) [58] and SHELXL-97(for **C₄**) [59] by full-matrix least-squares on F^2. The positions of hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program for compounds **C₁**, **C₃**, **C₄**, **C₅** [60].

2.2. Spectroscopic measurements

^{1}H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra were recorded on a FT-NMR, Bruker Avance DRS 500 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to TMS. ^{31}P and ^{119}Sn chemical shifts were measured relative to 85% H_3PO_4 and $Sn(CH_3)_4$ as external standards respectively. Infrared (IR and FTIR) spectra were recorded on a Shimadzu model IR-60 and FTIR (Thermo Nicolet) Nexus 870 spectrometers. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

2.3. Syntheses

After refluxing of phosphorus pentachloride and nicotinamide ($C_5H_4NC(O)NH_2$) in 1:1 molar ratio in CCl_4 for 6 h, solution let to get cold to the room temperature. Then formic acid was syringed drop-wise into the vigorously stirring solution in 15 min and let to stir for 6 h. Resulting white precipitate A, was filtered and dried. Precipitate B, was also prepared from the reaction of phosphorus pentachloride with Isonicotinamide exactly similar to the procedure used to produce A.

2.3.1. N-nicotinyl, N′,N″-bis(tert-butyl) phosphoric triamide

2.3.1.1. $C_5H_4NC(O)NHP(O)[NHC(CH_3)_3]_2$ (***L₁***). Compound **L₁** was synthesized from the reaction of precipitate A with *t*-butyl amine in 1:4 molar ratio of nicotinamide (initiator): corresponding amine. The mentioned amine was added drop-wise to a mixture of reaction in acetonitrile (40 mL) while stirring. The temperature was not allowed to rise above 4 °C. After stirring for 8 h and then evaporating the solvent, the residue was washed with distilled H_2O.

Yield (mol): 72%. Elemental Anal. Calc. for: C, 53.85; H, 8.01; N, 17.95. Found: C, 53.70; H, 8.03; N, 17.99%. IR (KBr, cm^{-1}): $\bar{\nu}$ = 3320(m, NH), 3120(m), 2950(m, CH_2), 1636(vs, C═O), 1584(m, ν_{ring}), 1441(s, δ_{CH}), 1405(s), 1287(m, ν_{ring}), 1237(s, P═O), 1205(s), 1117(w), 1014(s, ν_{ring}), 886(m), 850(w), 803(m), 730(m), 584(m), 530(m), 488(w). ^{1}H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 1.21(m, 18H), 4.06(d, ^{2}J(PNH) = 7.1 Hz, 2H, NH_{amine}), 7.47(dd, ^{3}J(H,H) = 7.8 Hz, ^{3}J(H,H) = 4.8 Hz, 1H), 8.29(d, ^{3}J(H,H) = 7.9 Hz, 1H), 8.70(d, ^{3}J(H,H) = 4.7 Hz, 1H), 9.07(d, ^{5}J(P,H) = 2.1 Hz, 1H), 9.72(s, 1H, NH_{amide}). ^{13}CNMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 31.16(d, ^{3}J(P,C) = 4.9 Hz), 50.35(s), 123.25(s), 129.70(d, ^{3}J(P,C) = 7.9 Hz, C_{ipso}), 135.49(s), 149.02(s), 152.23(s), 166.77(s, C═O). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 3.66 (m). UV–Vis in methanol: λ_{max} = 240 nm.

2.3.2. N-nicotinyl, N′,N″-bis(cyclohexyl) phosphoric triamide

2.3.2.1. $C_5H_4NC(O)NHP(O)[NH(C_6H_{11})]_2$ (***L₂***). Compound **L₂** was synthesized and purified in the same way that was used for **L₂**, using cyclohexylamine instead of *t*-butyl amine.

Yield (mol): 89%. Elemental Anal. Calc. for: C, 59.34; H, 7.97; N, 15.38. Found: C, 59.19; H, 7.99; N, 15.42%. FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3285(s, NH), 2925(s, CH_2), 2852(ms), 1644(s, C═O), 1587(ms, ν_{ring}), 1485(ms), 1455(m), 1423(s, δ_{CH}), 1343(mw), 1295(mw), 1279(m, ν_{ring}), 1215(ms, P = O), 1185(m), 1118(mw), 1096(s), 1024(mw), 1002(m), 929(mw), 912(m), 883(m), 842(mw), 790(m), 756(mw), 709(m), 688(mw), 618(mw), 569(m), 523(m), 482(mw), 438(w), 410(w). ^{1}H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 1.14(m, 10H), 1.45(d, ^{3}J(H,H) = 11.8 Hz, 2H), 1.60(m, 4H), 1.75(m, 4H), 2.94(m, 2H), 4.21(dd, ^{2}J(PNH) = 9.5 Hz, ^{3}J(H,H) = 9.2 Hz, 2H, NH_{amine}), 7.49(dd, ^{3}J(H,H) = 7.9 Hz, ^{3}J(H,H) = 4.8 Hz,1H), 8.27(d, ^{3}J(H,H) = 8.0 Hz, 1H), 8.71(dd, ^{3}J(H,H) = 4.0 Hz, ^{7}J(P,H) = 1.2 Hz,1H), 9.06(d, ^{5}J(P,H) = 1.5 Hz, 1H, Ha), 9.59(s, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 24.68(d, J(P,C) = 10.1 Hz), 25.07(s), 34.91(d, ^{3}J(P,C) = 4.0 Hz), 35.18(d, ^{3}J(P,C) = 6.1 Hz), 49.29(s), 123.32(s), 129.52(d, ^{3}J(P,C) = 7.7 Hz, C_{ipso}), 135.49(s), 148.95(s), 152.33(s), 166.60(s, C = O). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 7.08 (m). UV–Vis in methanol: λ_{max} = 259.5 nm.

2.3.3. N-isonicotinyl, N′,N″-bis(cyclohexyl) phosphoric triamide

2.3.3.1. $C_5H_4NC(O)NHP(O)[NH(C_6H_{11})]_2$ (***L₃***). A mixture of cyclohexyl amine, (2 mmol, 0.23 mL), and triethylamine, (2 mmol, 0.28 mL), was added drop-wise to a solution of precipitate B (0.239 g) in chloroform (35 mL) at 0 °C and stirred for 72 h. After evaporating the solvent, the residue was washed with distilled H_2O.

Yield (mol): 67%. Elemental Anal. Calc. for: C, 59.34; H, 7.97; N, 15.38. Found: C, 59.19; H, 7.99; N, 15.32%. FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3315(s), 3248(s), 2926, 2854(s), 1661(s, C═O), 1556(mw), 1496(mw), 1455(s), 1434(s), 1410(mw), 1271(mw), 1200(s, P═O), 1185(mw), 1110(s), 1071(w), 1068(w), 1002(w), 930(w), 915(mw), 884(mw), 798(mw), 791(mw), 759(mw), 681, 661(w), 579(w), 548(w), 518(w), 485(w)cm^{-1}. ^{1}H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 1.29(m, 10H), 1.46(d, ^{3}J(H,H) = 11.8 Hz, 2H), 1.60 (m, 4H), 1.74 (dd, ^{2}J(H,H) = 28.2 Hz, ^{4}J(P,H) = 2.4 Hz, 4H), 2.93(m, 2H), 2.22 (dd, ^{2}J(PNH) = 9.3 Hz, ^{3}J(H,H) = 9.5, 2H, NH_{amin}), 7.82 (dd, ^{3}J(H,H) = 5.9 Hz, ^{6}J(P,H) = 1.6 Hz, 2H), 8.71(m, 2H), 9.61(s, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 166.46(s, C═O), 150.14(s), 140.92 (d, ^{3}J(P,C) = 8.0 Hz), 121.47(s), 49.24(s), 35.14 (d, ^{3}J(P,C) = 6.1 Hz), 34.85 (d, ^{3}J(P,C) = 4.1 Hz), 25.03(s), 24.62(d, J(P,C) = 9.4 Hz). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm):δ = 6.84 (m). UV–Vis in ethanol: λ_{max} = 201.8 nm.

2.3.4. N-isonicotinyl, N′,N″-bis(t-butyl) phosphoric triamide

2.3.4.1. $C_5H_4NC(O)NHP(O)[NHC(CH_3)_3]_2$ (***L₄***). This ligand was prepared as our previous reported pathway [18].

Yield (mol): 65%. Elemental Anal. Calc. for: C, 53.85; H, 8.01; N, 17.95. Found: C, 53.69; H, 8.03; N, 18.01%. FTIR (KBr, cm^{-1}):

$\bar{\nu}$ = 3386(w), 2967(mw), 1673(s, C=O), 1602(w), 1560(mw), 1505(mw), 1441(s), 1387(s), 1361(mw), 1282(mw), 1227(s), 1197(s), 1119(w), 1048(s), 1017(s), 887(mw), 850(mw), 820(mw), 757(mw), 695(mw), 573(mw), 548(mw), 493(w), 433(w) cm^{-1}. ^1H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 1.21(s, 18H, *tert*-C_4H_9), 4.06(d, ^2J(PNH) = 7.3 Hz, 2H, NH_{amin}), 7.84(m, 2H), 8.70(m,2H), 9.79(d, ^2J(PNH) = 4.4, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm):δ = 166.61(s, C=O), 150.07(s), 141.12(d, ^3J(P,C) = 8.2 Hz), 121.53(s), 50.34(s), 31.12(d, ^3J(P,C) = 4.9 Hz). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 2.16 (b). UV–Vis in methanol: λ_{max} = 202 nm.

2.3.5. Bis[N-nicotinyl, N′,N″-bis(t-butyl) phosphoric triamide] dimethyl stannate(IV) dichloride (**C_1**)

2.3.5.1. $Sn(CH_3)_2Cl_2\{C_5H_4NC(O)NHP(O)[NH–C(CH)_3]_2\}_2$. *N*-nicotinyl, *N*′,*N*″-bis(*t*-butyl) phosphoric triamide (0.5 mmol, 0.156 g) was added to a solution of dimethyltin(IV) dichloride (0.25 mmol 0.055 g) in hot methanol (20 mL) and stirred at room temperature. After 14 days, the solvent was evaporated to give a white powder. Recrystallization in methanol–chloroform produced single crystals of **C_1**.

Yield (mol): 89%. Elemental Anal. Calc. for: C, 42.67; H, 6.16; N, 13.27. Found: C, 42.54; H, 6.17; N, 13.29%. IR (KBr, cm^{-1}): $\bar{\nu}$ = 3345(s), 3160(m), 2970(m), 1683(s, C=O), 1583(m), 1456(vs, δ_{CH}), 1408(s), 1387(m), 1362(m), 1275(m, ν_{ring}), 1225(s, P=O), 1204(m), 1144(vs), 1119(m), 1067(m), 1017(s), 880(m), 844(mw), 800(m), 744(mw), 707(m), 681(w), 612(w), 561(m, Sn–C), 475(mw, Sn–O), 412(mw, γ_{ring}). ^1H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 0.92–1.14{[d, $^2J(^{119}Sn,H)$ = 114.0 Hz], [d, $^2J(^{117}Sn,H)$ = 110.8 Hz], [s], 6H, CH_3–Sn}, 1.21(s, 18H), 4.04(d, ^2J(PNH) = 7.1 Hz, 2H, NH_{amine}), 7.47(dd, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 4.7 Hz, 1H), 8.29(d, ^3J(H,H) = 8.5 Hz, 1H), 8.71(d, ^3J(H,H) = 4.4 Hz, ^{1}H), 9.08(d, ^5J(P,H) = 1.4 Hz, 1H), 9.78(s,1H, NH_{amide}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 22.47(s, CH_3–Sn), 31.17(d, ^3J(P,C) = 4.9 Hz), 50.37(s), 123.25(s), 129.71(d, ^3J(P,C) = 7.9 Hz, C_{ipso}), 135.51(s), 149.03(s), 152.23(s), 166.77(s, C=O). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 2.45 (m). ^{119}Sn NMR (112.06 MHz, d_6-DMSO, 25 °C) (ppm): δ = −166.77(s). UV–Vis in methanol: λ_{max} = 250.8 nm.

2.3.6. Bis[N-nicotinyl, N′,N″-bis(cyclohexyl) phosphoric triamide] dimethyl stannate(IV) dichloride (**C_2**)

2.3.6.1. $Sn(CH_3)_2Cl_2\{NC_5H_4C(O)NHP(O)[NHC_6H_{11}]_2\}_2$. *N*-nicotinyl, *N*′,*N*″-bis(*cyclohexyl*) phosphoric triamide (0.4 mmol, 0.146 g) was added to a solution of dimethyltin(IV) dichloride (0.2 mmol 0.044 g) in hot ethanol (10 mL) and stirred for 7 days. After adding 5 mL of chloroform to the solution, solvents were evaporated slowly at room temperature to give the product.

Yield (mol): 86%. Elemental Anal. Calc. for: C, 48.42; H, 6.16; N, 11.89. Found: C, 48.31; H, 6.17; N, 11.93%. FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3309(m), 3285(m), 2925(ms, CH_2), 2854(m), 1649(s, C=O), 1589(m, ν_{ring}), 1487(m), 1455(s), 1443(s), 1417(s), 1277(m), 1202(ms, P=O), 1184(ms), 1110(s), 1023(mw), 1002(mw), 915(m), 883(m), 799(m), 735(w), 708(m), 680(m), 619(mw), 571(mw), 549(mw), 512(mw), 482(mw), 441(mw), 431(mw), 415(mw). ^1H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 0.46–0.61{[d, $^2J(^{119}Sn,H)$ = 71.2 Hz], [d, $^2J(^{117}Sn,H)$ = 68.2 Hz], [s], 6H, CH_3–Sn}, 1.16(m, 10H), 1.46(d, ^3J(H,H) = 11.6 Hz, 2H), 1.59(m, 4H), 1.75(m, 4H), 2.95(m, 2H), 4.19(m, 2H, NH_{amine}), 7.49(dd, ^3J(H,H) = 7.9 Hz, ^3J(H,H) = 4.8 Hz, 1H), 8.25(d, ^3J(H,H) = 7.9 Hz, 1H), 8.70(d, ^3J(H,H) = 3.9 Hz, 1H), 9.05(s, 1H), 9.52(s, 1H, NH_{amide}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 23.72(s, CH_3–Sn), 24.73(d, J(P,C) = 9.3 Hz), 25.13(s), 30.32(s), 34.98(d, ^3J(P,C) = 3.7 Hz), 35.22(d, ^3J(P,C) = 6.0 Hz), 49.35(d, ^2J(P,C) = 6.3 Hz), 123.36(s), 129.66(s, C_{ipso}), 135.54(s), 148.98(s), 152.34(s), 166.64(s, C=O). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 5.68(m). ^{119}Sn NMR (112.06 MHz, d_6-DMSO, 25 °C) (ppm): δ = −166.77(s). UV–Vis in methanol: λ_{max} = 245.4 nm.

2.3.7. Bis[N-isonicotinyl, N′,N″-bis(cyclohexyl) phosphoric triamide] dimethyl stannate(IV) dichloride (C_3)

2.3.7.1. $Sn(CH_3)_2Cl_2\{NC_5H_4C(O)NHP(O)[NHC_6H_{11}]_2\}_2$. *N*-isonicotinyl, *N*′,*N*″-bis(cyclohexyl) phosphoric triamide (0.2 mmol, 0.073 g) was added to a solution of dimethyltin(IV) dichloride (0.1 mmol 0.022 g) in hot ethanol (3 mL) and stirred for 30 min. Then the solvent was evaporated slowly at room temperature to give the single crystals of the product.

Yield (mol): 95%. Elemental Anal. Calc. for: C, 48.42; H, 6.16; N, 11.89. Found: C, 48.29; H, 6.17; N, 11.86%. FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3346(mw), 3185(mw), 2928(mw), 2851(mw), 1946(w), 1676(s, C=O), 1596(w), 1559(w), 1505(w), 1452(s), 1303(w), 1271(w), 1238(w), 1163(m, P=O), 1092(s), 1033(mw), 997(mw), 946(w), 916(w), 889(w), 846(w), 820(w), 787(w), 757(w), 707(w), 653(w), 574(w), 518(mw) cm^{-1}. ^1H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 0.92–1.22(m, 13H), 1.45–1.88(m, 10H), 2.94(b, 2H), 4.23(t, ^2J(PNH) = 9.2 Hz, ^3J(H,H) = 8.9 Hz, 2H, NH_{amin}), 7.81(s, 2H), 8.71(s, 2H), 9.57(s, NH_{amide}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 23.65(s), 24.68(d, J(P,C) = 9.1 Hz), 25.08(s), 30.28(s), 34.90(s), 35.18(d,^3J(P,C) = 5.9 Hz), 49.27(s), 121.52(s), 140.99(s,), 150.19(s), 166.49(s, C=O). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 5.48(m, b). ^{119}Sn NMR (112.06 MHz, d_6-DMSO, 25 °C) (ppm): δ = −238.25(s). UV–Vis in ethanol: λ_{max} = 206 nm.

2.3.8. Bis[N-isonicotinyl, N′,N″-bis(t-butyl) phosphoric triamide] dimethyl stannate(IV) dichloride (**C_4**)

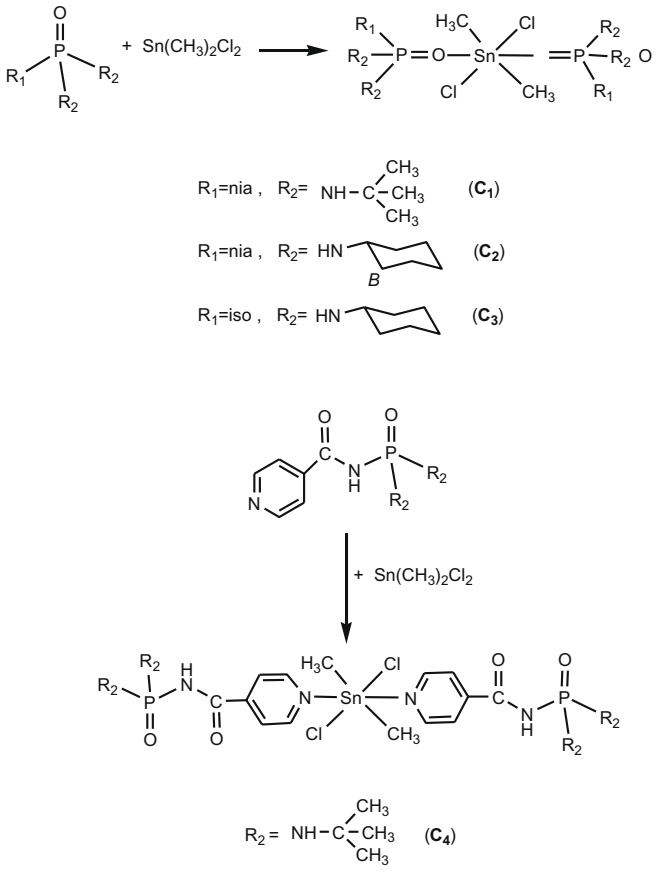
2.3.8.1. $Sn(CH_3)_2Cl_2\{NC_5H_4C(O)NHP(O)[NHC(CH_3)_3]_2\}_2$. *N*-isonicotinyl, *N*′,*N*″-bis(*t*-butyl) phosphoric triamide (0.2 mmol, 0.062 g) was added to a solution of dimethyltin(IV) dichloride (0.1 mmol 0.022 g) in hot ethanol (3 mL) and stirred at room temperature. After 30 min, 1 mL of acetonitrile was added to the reaction vessel and single crystals of **C_4** were obtained by slow evaporation of the solvents at room temperature.

Yield (mol): 95%. Elemental Anal. Calc. for: C, 42.67; H, 6.16; N, 13.27. Found: C, 42.80; H, 6.14; N, 13.31%. FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3385(mw), 3346(mw), 3116(w), 3044(w), 2972(mw), 2923(w), 1979(w), 1882(w), 1667(s), 1617(w), 1556(w), 1512(mw), 1445(s), 1386(mw), 1361(s), 1335(w), 1290(mw), 1221(s), 1199(s), 1125(w), 1063(mw), 1045(mw), 1016(vs), 896(mw), 867(mw), 854(mw), 815(mw), 766(mw), 695(mw), 678(mw), 588(mw), 568(w), 526(mw), 490(w), 433(w), 414(w) cm^{-1}. ^1H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 0.91–1.1 [0.91(d, $^2J(^{119}Sn,H)$ = 114.28 Hz), 0.92(d, $^2J(^{117}Sn,H)$ = 107.98 Hz), 1.03(s), 6H], 1.21(s, 36H), 4.06(d, ^2J(PNH) = 7.35 Hz, 4H, NH_{amin}), 7.83(dd, ^3J(H,H) = 5.8 Hz, ^5J(P,H) = 1.5 Hz, 4H), 8.71(d, ^3J(H,H) = 5.5 Hz, 4H), 9.78(d, ^2J(PNH) = 6.5 Hz, 2H, NH_{amid}). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 22.37(s), 31.16(d, ^3J(P,C) = 4.8 Hz), 50.38(s), 121.58(s), 141.15(d, ^3J(P,C) = 8.0 Hz), 150.12(s), 166.65(s, C=O). ^{31}P NMR (202.46 MHz, d_6-DMSO, 25 °C, H_3PO_4 external) (ppm): δ = 2.18(m). ^{119}Sn NMR (112.06 MHz, d_6-DMSO, 25 °C) (ppm): δ = −238.26(s). UV–Vis in ethanol: λ_{max} = 206.4 nm.

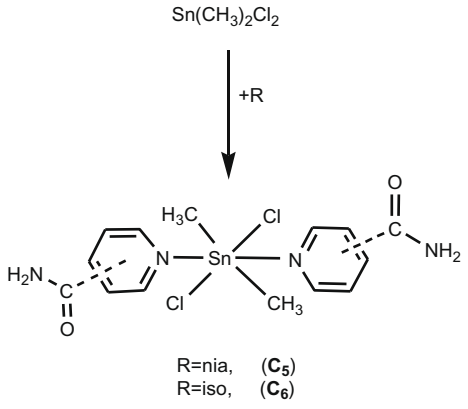
2.3.9. Bis(nicotinamide) dimethyl stannate(IV) dichloride (**C_5**)

2.3.9.1. $Sn(CH_3)_2Cl_2\{NC_5H_4C(O)NH_2\}_2$. Nicotinamide (1 mmol, 0.122 g) was added to a solution of dimethyltin(IV) dichloride (0.5 mmol 0.11 g) in ethanol (20 mL) and stirred at room temperature. After 7 days, the solvent was concentrated and 5 mL of *n*-heptane was added to the reaction vessel. The single crystals of **C_5** were obtained during 7 days by slow evaporation of the solvents.

Yield (mol): 94%. Elemental Anal. Calc. for: C, 36.23; H, 3.88; N, 12.08. Found: C, 36.12; H, 3.87; N, 12.05%. IR (KBr, cm^{-1}): $\bar{\nu}$ = 3445(s), 3350(s, NH), 3290(ms), 3090(m), 1682(vs, C=O), 1600(s, NH_{2-scis}), 1578(ms, ν_{ring}), 1469(m), 1405(s), 1425(m), 1384(m), 1359(s, δ_{CH}), 1321(m), 1193(m), 1145(m), 1140(ms), 1085(m), 1047(s), 961(w), 895(w), 830(mw), 771(ms), 738(s), 692(ms), 641(s), 612(ms), 564(mw), 519(s, Sn–C), 468(mw), 424(mw). ^{1}H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 0.9–1.13{[d, $^2J(^{119}Sn,H)$ = 113.5 Hz], s, 6H, CH_3–Sn}, 7.46(s, 2H, NH), 7.56(s, 2H, NH), 8.14–8.17(m, 4H, Ar–H), 8.66(S, 2H), 9.01(S, 2H). ^{13}C NMR (125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 22.54(s, CH_3), 123.33(s), 129.65(s), 135.10(s), 148.63(s), 151.81(s), 166.43(s, C=O). ^{119}Sn NMR (112.06 MHz, d_6-DMSO, 25 °C) (ppm): δ = −166.76(s). UV–Vis in methanol: λ_{max} = 254.5 nm.



Scheme 1. Preparation pathway of organotin(IV) phosphoramidate complexes $\mathbf{C_1}$–$\mathbf{C_4}$.



Scheme 2. Preparation pathway of organotin(IV) nicotinamide and isonicotinamide complexes $\mathbf{C_5}$ and $\mathbf{C_6}$.

2.3.10. Bis(isonicotinamide) dimethyl stannate(IV) dichloride ($\mathbf{C_6}$)

2.3.10.1. $Sn(CH_3)_2Cl_2\{NC_5H_4C(O)NH_2\}_2$. Isonicotinamide (0.2 mmol, 0.024 g) was added to a solution of dimethyltin(IV) dichloride (0.1 mmol 0.022 g) in hot ethanol (3 mL) and stirred for 30 min. Then the solvent was evaporated slowly at room temperature to give the product $\mathbf{C_6}$.

Yield (mol): 98%. Elemental Anal. Calc. for: C, 36.23; H, 3.88; N, 12.08. Found: C, 36.14; H, 3.89; N, 12.06%. FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3361(mw), 3299(mw), 3252(mw), 3191(mw), 3100(w), 1940(w), 1667(vs, C=O), 1624(s), 1609(s), 1555(s), 1424(s), 1393(s), 1224(mw), 1144(w), 1122(w), 1067(mw), 1017(s), 965(w), 851(mw), 795(mw), 764(mw), 622(s), 572(mw), 517(w), 424(w) cm^{-1}. ^{1}H NMR (500.13 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 0.91–1.14 [0.91(d, $^2J(^{119}Sn,H)$ = 112.9 Hz), 0.92(d, $^2J(^{117}Sn,H)$ = 108.9 Hz), 1.03(s), 6H], 7.67(s, 1H, NH_{amin}), 7.75(d, $^3J(H,H)$ = 5.5, 2H), 8.21(s, 1H, NH_{amin}), 8.69(d, $^3J(H,H)$ = 5.5, 2H). ^{13}C NMR 125.76 MHz, d_6-DMSO, 25 °C, TMS) (ppm): δ = 22.32(s), 121.27(s), 141.21(s), 150.07(s), 166.20(s, C=O). ^{119}Sn NMR

Table 1
Spectroscopic NMR data of compounds $\mathbf{L_1}$–$\mathbf{L_4}$ and $\mathbf{C_1}$–$\mathbf{C_4}$.

Compound	^nJ(P,H) (Hz)	$\delta(^{31}P)$ (ppm)	$^2J(PNH)_{amide}$ (Hz)	$^3J(P,C)_{amide}$ (Hz)
$\mathbf{L_1}$	2.1 (for n = 5)	3.66	–	7.9
$\mathbf{C_1}$	1.4 (for n = 5)	2.45	–	7.9
$\mathbf{L_2}$	1.5 (for n = 5) 1.2 (for n = 7)	7.08	–	7.7
$\mathbf{C_2}$	–	5.68	–	–
$\mathbf{L_3}$	1.6 (for n = 5)	6.84	–	8.0
$\mathbf{C_3}$	–	5.48	–	–
$\mathbf{L_4}$[a]	1.6 (for n = 5)	2.18	4.4	8.2
$\mathbf{C_4}$	1.5 (for n = 5)	2.18	6.6	8.0

[a] From Ref. [18].

Table 2
Spectroscopic IR and UV data of compounds $\mathbf{L_1}$–$\mathbf{L_4}$ and $\mathbf{C_1}$–$\mathbf{C_4}$.

Compound	ν(C=O) (cm^{-1})	ν(P=O) (cm^{-1})	$\nu^a_{pyridine}$ (cm^{-1})	$\delta^b_{pyridine}$ (cm^{-1})	λ_{max} (nm)
$\mathbf{L_1}$	1636	1237	1584	606	240
$\mathbf{C_1}$	1683	1225	1583	612	250.8
$\mathbf{L_2}$	1644	1215	1587	618	259.5
$\mathbf{C_2}$	1649	1202	1589	619	245.4
$\mathbf{L_3}$	1661	1200	1595	579	201.8
$\mathbf{C_3}$	1676	1163	1596	574	206
$\mathbf{L_4}$[c]	1673	1227	1602	573	202
$\mathbf{C_4}$	1667	1221	1614	588	206.4

[a] Ring stretching of pyridine.
[b] Planar ring deformation of pyridine.
[c] From Ref. [18].

Table 3
Spectroscopic data of compounds nicotinamide, isonicotinamide and their Sn(IV) complexes $\mathbf{C_5}$, $\mathbf{C_6}$.

Compound	ν(C=O) (cm^{-1})	$\nu_{pyridine}$ (cm^{-1})	$\delta_{pyridine}$ (cm^{-1})	$\gamma_{pyridine}$ (cm^{-1})	λ_{max} (nm)
Nicotinamide	1674	1570	592	405	6
$\mathbf{C_5}$	1682	1578	612	424	254.5
Isonicotinamide	1622	1594	537	407	281.2
$\mathbf{C_6}$	1667	1609	572	424	278.8

(112.06 MHz, d_6-DMSO, 25 °C) (ppm): δ = −238.26(s). UV–Vis in ethanol: λ_{max} = 278.8 nm.

3. Results and discussion

3.1. NMR and IR study

Synthesis of compounds **L_1**–**L_3** were performed according to Section 2 and organotin complexes **C_1**–**C_6** were obtained from the reaction of **L_1**–**L_4**, nicotinamide and isonicotinamide with dimethyltin(IV) dichloride (Schemes 1 and 2).

Some selected spectroscopic data of the synthesized compounds are listed in Tables 1–3. As it can be seen from Table 1, chemical shift of ^{31}P for compounds **L_1**–**L_4** is in the range of 2.18–7.08 ppm. ^{31}PNMR spectra indicate that by coordinating to Sn, this parameter shows a small shift (at most 1.5 ppm) to up fields.

^{1}H NMR spectra showed that $^2J(PNH)_{amide}$ is observed only for **L_4** and its Sn complex **C_4**. This is likely due to the different binding

Table 4
Crystallographic data for complexes **C_1**, **C_3**, **C_4** and **C_5**.

	C_1	**C_3**	**C_4**	**C_5**
Empirical formula	$C_{30}H_{56}Cl_2N_8O_4P_2Sn$	$C_{38}H_{64}Cl_2N_8O_4P_2Sn$	$C_{30}H_{56}Cl_2N_8O_4P_2Sn$	$C_{14}H_{18}Cl_2N_4O_2Sn$
Formula weight	844.36	948.50	844.36	463.91
T (K)	100(2)	120(2)	100(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P\,2_1/c$
Unit cell dimensions				
a (Å)	9.1505(10)	10.1588(7)	7.7734(2)	7.0576(5)
b (Å)	10.3408(5)	10.2135(7)	10.5867(3)	16.519(1)
c (Å)	11.9147(6)	12.3594(8)	12.4205(4)	7.2637(5)
α (°)	114.6320(10)	72.1300(10)	85.7896(5)	90
β (°)	104.3580(10)	79.8540(10)	88.4260(5)	90.083
γ (°)	93.1890(10)	69.1710(10)	81.6217(5)	90
V (Å^3)	976.49(13)	1137.50(13)	1008.36(5)	846.8(1)
Z, calculated density (Mg m^{-3})	1, 1.436	1, 1.385	1, 1.390	2, 1.819
Absorption coefficient (mm^{-1})	0.917	0.796	0.888	1.838
F(0 0 0)	438	494	438	460
Crystal size (mm)	0.23 × 0.15 × 0.08	0.55 × 0.40 × 0.25	0.17 × 0.15 × 0.15	0.52 × 0.34 × 0.20
θ Range for data collection (°)	1.97–30.03°	2.21–26.00°	1.64–30.00°	2.47–29.00°
Limiting indices	$-12 \leqslant h \leqslant 12$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$	$-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-15 \leqslant l \leqslant 15$	$-10 \leqslant h \leqslant 10$, $-14 \leqslant k \leqslant 14$, $-17 \leqslant l \leqslant 17$	$-9 \leqslant h \leqslant 9$, $-22 \leqslant k \leqslant 22$, $-9 \leqslant l \leqslant 9$
Reflections collected	12 849	10 051	17 654	8460
Independent reflections	5691 [R_{int} = 0.0221]	4442 [R_{int} = 0.0214]	5862 [R_{int} = 0.0230]	2240 [R_{int} = 0.0242]
Completeness to θ (%)	99.8	99.3	99.9	99.4
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Maximum and minimum transmission	0.9303 and 0.8168	0.810 and 0.675	0.878 and 0.864	0.692 and 0.438
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5691/0/221	4442/0/251	5862/0/224	2240/0/108
Goodness-of-fit (GOF) on F^2	1.012	1.007	1.003	1.088
Final R indices	R_1 = 0.0219, wR_2 = 0.0574	R_1 = 0.0246, wR_2 = 0.0634	R_1 = 0.0214, wR_2 = 0.0535	R_1 = 0.0223, wR_2 = 0.0502
R indices (all data)	R_1 = 0.0244, wR_2 = 0.0588	R_1 = 0.0257, wR_2 = 0.0645	R_1 = 0.0231, wR_2 = 0.0544	R_1 = 0.0282, wR_2 = 0.0543
Largest difference in peak and hole (e Å^{-3})	0.633 and −0.838	0.978 and −0.720	0.808 and −0.529	0.644 and −0.433

Table 5
Selected bond lengths (Å) for compounds **C_1**, **C_3** and **C_4**.

C_1		**C_3**		**C_4**	
Sn(1)–C(1)#1	2.1157(13)	Sn(1)–C(1)#1	2.1150(19)	Sn(1)–C(15)#1	2.1222(13)
Sn(1)–C(1)	2.1157(13)	Sn(1)–C(1)	2.1150(19)	Sn(1)–C(15)	2.1222(13)
Sn(1)–O(1)	2.2360(9)	Sn(1)–O(1)	2.1941(12)	Sn(1)–N(4)	2.3893(10)
Sn(1)–O(1)#1	2.2360(9)	Sn(1)–O(1)#1	2.1941(12)	Sn(1)–N(4)#1	2.3893(10)
Sn(1)–Cl(1)	2.5816(3)	Sn(1)–Cl(1)#1	2.5860(4)	Sn(1)–Cl(1)#1	2.5567(3)
Sn(1)–Cl(1)#1	2.5816(3)	Sn(1)–Cl(1)	2.5860(4)	Sn(1)–Cl(1)	2.5567(3)
P(1)–O(1)	1.5010(9)	P(1)–O(1)	1.4949(13)	P(1)–O(1)	1.4810(9)
P(1)–N(1)	1.6946(11)	P(1)–N(1)	1.6902(15)	P(1)–N(1)	1.6966(11)
P(1)–N(2)	1.6159(11)	P(1)–N(3)	1.6109(15)	P(1)–N(2)	1.6309(11)
P(1)–N(3)	1.6186(11)	P(1)–N(4)	1.6163(15)	P(1)–N(3)	1.6330(11)
O(2)–C(2)	1.2184(16)	O(2)–C(2)	1.218(2)	O(2)–C(1)	1.2267(15)
N(1)–C(2)	1.3719(16)	N(1)–C(2)	1.368(2)	N(1)–C(1)	1.3583(15)
N(1)–H(1)	0.9200	N(1)–H(1N)	0.9016	N(1)–H(1N)	0.9003
N(2)–C(12)	1.4874(17)	N(3)–C(8)	1.477(2)	N(2)–C(7)	1.4835(16)
N(2)–H(2)	0.9199	N(3)–H(3N)	0.8257	N(2)–H(2N)	0.9002
N(3)–C(8)	1.4892(17)	N(4)–C(14)	1.475(2)	N(3)–C(11)	1.4882(17)
N(3)–H(3)	0.9200	N(4)–H(4N)	0.7833	N(3)–H(3N)	0.9003

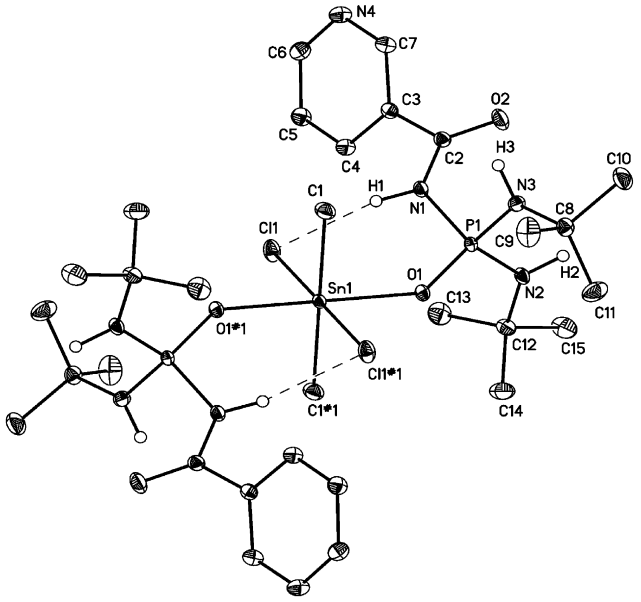


Fig. 2. Molecular structure and atom labeling scheme for $\mathbf{C_1}$ (50% probability ellipsoids).

properties of the substituted groups on phosphorus atom. The mentioned $^2J(PNH)_{amide}$ in $\mathbf{C_4}$ is 6.6 Hz which has been increased relative to its ligand's (Table 1). Such large variation in this coupling constant, which is because of the complexation, is accompanied with a negligible changing in P–N_{amide} bond length (from 1.6971 Å in $\mathbf{L_4}$ [18] to 1.6966 Å in $\mathbf{C_4}$, Table 5).

^{1}H NMR spectra of compounds $\mathbf{L_1}$–$\mathbf{L_4}$ demonstrated long-range $^nJ_{P,H}$ (n = 5, 6, 7) coupling constants in the range of 1.2–2.1 Hz which have been reduced or vanished by coordinating to Sn in complexes $\mathbf{C_1}$–$\mathbf{C_4}$ (Table 1). Such interesting couplings have been observed only in few compounds up to now [30–36]. Different explanations have been presented in some articles to describe

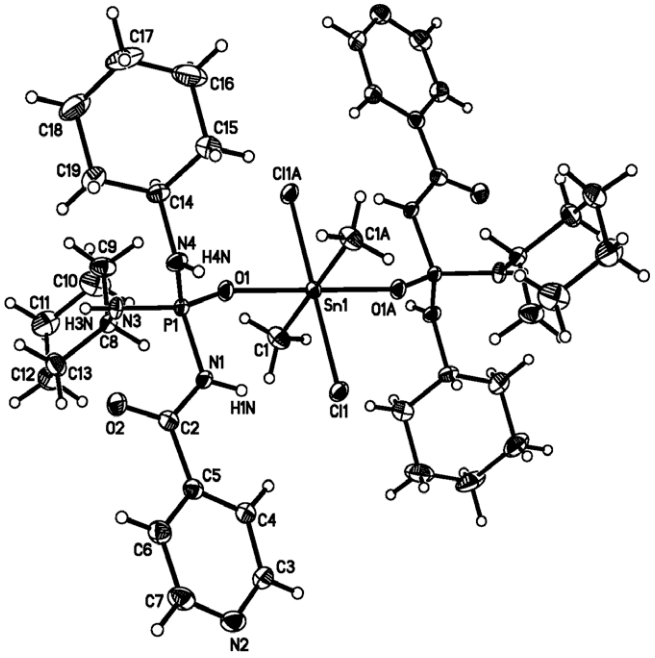


Fig. 3. Molecular structure and atom labeling scheme for $\mathbf{C_3}$ (50% probability ellipsoids).

appearing or disappearing of P–H long-range couplings; such as Fermi contact interactions [34], stereochemical and structural effects [30–33], "ground-state hyperconjugation" or "σ–π configuration interactions" [35], angular overlap model [35] and partial multiple bonds formation [30]. ^{1}H NMR spectra of molecules $\mathbf{C_1}$–$\mathbf{C_6}$ showed the Sn(IV) satellites with $^2J(^{119}Sn, H)$ in the range of 71.2–114.9 Hz. No coupling between ^{117}Sn and H nuclei was observed for $\mathbf{C_5}$ while the value of $^2J(^{117}Sn, H)$ in other complexes varies from 68.2 Hz in $\mathbf{C_2}$ to 110.8 Hz in $\mathbf{C_1}$.

^{13}C NMR spectra of the compounds containing *t*-butylamine ($\mathbf{L_1}$, $\mathbf{L_4}$, $\mathbf{C_1}$, $\mathbf{C_4}$) revealed that no remarkable changing is occurred in chemical shifts of carbons or their $^nJ(P,C)$ coupling constants by coordinating to Sn. Compounds $\mathbf{L_2}$, $\mathbf{L_3}$ showed five different chemical shifts for their cyclohexyl amine rings .This is due to the different dihedral angles between P=O and C_α–C_β (see Scheme 1) which causes unequal $^3J(P,C)_{amine}$ for these two C_β carbons. Such inequity for cyclohexyl amine carbons has been reported for similar phosphoramidates in one of our previous papers [37]. With coordinating of $\mathbf{L_2}$ to Sn, $^2J(P,C)_{amine}$ demonstrated a huge increasing (from zero in $\mathbf{L_2}$ to 6.3 Hz in $\mathbf{C_2}$) whereas not special varying in the $^3J(P,C)_{amine}$ is happened in $\mathbf{C_2}$. In $\mathbf{C_3}$ only one of the above-mentioned $^3J(P,C_\beta)_{amine}$ has been reduced to zero by forming the complex. In addition, for complexes $\mathbf{C_2}$, $\mathbf{C_3}$ all the cyclohexyl amine carbons are unequal and showed different signals in their ^{13}C NMR spectra.

IR spectra of $\mathbf{C_1}$–$\mathbf{C_3}$ showed a large decreasing for $\nu_{P=O}$ and increasing for $\nu_{C=O}$ in comparison to their related ligands while the main vibrational frequencies of the pyridine ring (ν, δ) are close to those values of their ligands' (Table 2).

This observation gave us an idea about coordinating from P=O site of the ligands to Sn in these complexes which was confirmed by the X-ray crystallographic structures for $\mathbf{C_1}$ and $\mathbf{C_3}$ (Figs. 2 and 3).

According to the reported observations, phosphoramidate compounds usually form organotin complex through their P=O site. This causes $\nu_{P=O}$ to become weaker than that of its related ligand while $\nu_{C=O}$ frequency gets stronger [38,39]. Although compounds $\mathbf{L_1}$–$\mathbf{L_3}$ have three active sites for coordination to metal (C=O, P=O and N of pyridine), this is attention-grabbing that P=O is still the most active site of coordination. It means that the behavior of these three phosphorylated nicotinamide and isonicotinamide with Sn is similar to that of other phosphoramidates. Interestingly some opposite results were observed for the mentioned frequencies of $\mathbf{L_4}$ and $\mathbf{C_4}$ (Table 2). The $\nu_{P=O}$ and $\nu_{C=O}$ values of these two compounds were very close to each other whereas the ring stretching and planar ring deformation of pyridine increased by complexation. It means coordinating of $\mathbf{L_4}$ to Sn is occurred from the N of pyridine. This is confirmed by the crystal structure of $\mathbf{C_4}$ (Fig. 4).

In the case of compounds $\mathbf{C_5}$, $\mathbf{C_6}$ the main above-mentioned frequencies of pyridine ring (Table 3) illustrated increased value in comparison to those of their ligands (nicotinamide and isonicotinamide). This is because of the coordinating to Sn from their $N_{pyridine}$ donor site which confirmed by X-ray crystallography for $\mathbf{C_5}$ (Fig. 5). The pyridine frequency variations for $\mathbf{C_4}$–$\mathbf{C_6}$, relative to their corresponding ligands, are in good agreement with those for the metal complexes of isonicotinamide and nicotinamide, when these amides act as $N_{pyridine}$ donor ligands [25,40].

In complexes $\mathbf{C_1}$–$\mathbf{C_6}$ the band about 549–574 cm^{-1} can be attributed to the stretching frequency of Sn–C bonds [41].

3.2. Electronic spectra study

The synthesized complexes $\mathbf{C_1}$–$\mathbf{C_6}$ and their related ligands, $\mathbf{L_1}$–$\mathbf{L_6}$ showed one intense absorption maximum in the range of 201.8–281.2 nm (UV region) which is in good conformity with the reported area for the pyridine derivatives [23,42,43]. A comparison

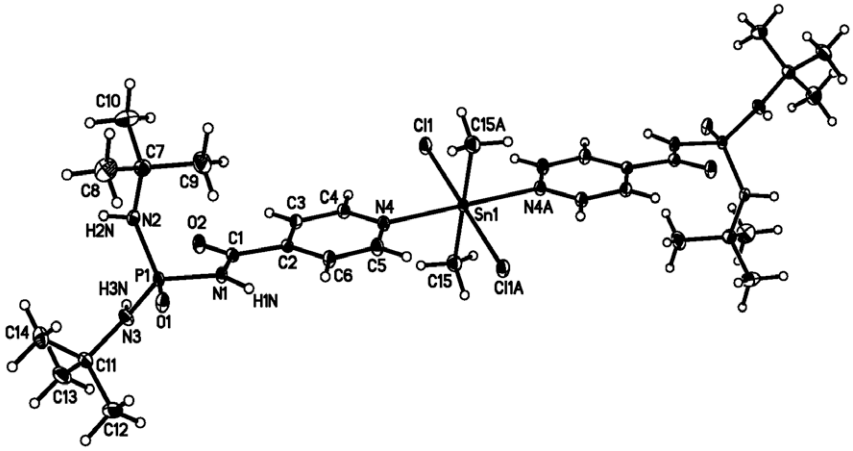


Fig. 4. Molecular structure and atom labeling scheme for complex $\mathbf{C_4}$ (50% probability ellipsoids).

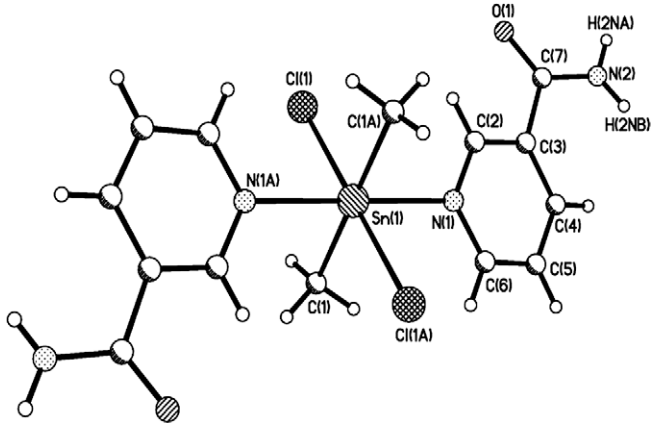


Fig. 5. Molecular structure and atom labeling scheme for $\mathbf{C_5}$ (50% probability ellipsoids).

between the UV–Vis data of $\mathbf{L_1}$–$\mathbf{L_6}$, nicotinamide, isonicotinamide and their corresponding complexes showed that by forming the organotin complexes a shift is occurred in the values of λ_{max} (Tables 2 and 3).

Researches have shown that when the electronic absorption measurement of pyridine is performed in a polar solvent the $\pi \rightarrow \pi^*$ transition bond is strongly intensified [44]. So we can assign the only intense observed absorption band for our compounds to $\pi \rightarrow \pi^*$ intraligand transitions.

3.3. X-ray crystallography investigation

Single crystals of compounds $\mathbf{C_1}$, $\mathbf{C_3}$, $\mathbf{C_4}$ and $\mathbf{C_5}$ were obtained after slow evaporation of mentioned solutions (see Section 2) at room temperature. The crystal data and the details of the X-ray analysis are given in Table 4, selected bond lengths and angles in Tables 5–7 and hydrogen bonding data in Table 8. Molecular structures of these compounds are shown in Figs. 2–5.

The central Sn atom in compounds $\mathbf{C_1}$, $\mathbf{C_3}$, $\mathbf{C_4}$ and $\mathbf{C_5}$ has octahedron coordination. Identical ligands (the two methyl groups, the two phosphoramidates and the two chlorine atoms) are in *trans* positions with the bond angles of 180.0° around Sn atom. The different ligands are *cis* to each other and C–Sn–O, C–Sn–Cl and O–Sn–Cl bond angles are about 90° (Tables 6 and 7). The Sn–C bond lengths in these complexes are 2.1157(13), 2.1222(13), 2.1150(19) and 2.126(2) Å, respectively, that are quite close to those reported in the literature [39,45]. The Sn–Cl bond lengths in $\mathbf{C_1}$, $\mathbf{C_3}$, $\mathbf{C_4}$, $\mathbf{C_5}$ are 2.5816(3), 2.5860(4), 2.5567(3) and 2.5799(5) Å correspondingly which are lying in the normal covalent radii 2.37–2.60 Å [46]. The Sn–O bond lengths in $\mathbf{C_1}$ and $\mathbf{C_3}$ are 2.2360(9) and 2.1941(12) Å respectively that are shorter than sum of the Van der Waals radii of Sn and O atoms (3.70 Å) [47].

Crystal structures of $\mathbf{C_4}$ showed that in contrast to the other two phosphoramidate derivatives ($\mathbf{C_1}$ and $\mathbf{C_3}$) coordination of ligand to Sn in this complex has been occurred from the nitrogen site of the pyridine ring just like $\mathbf{C_5}$ in which there is no P=O donor site in the molecule of its ligand. It seems that in these complexes there is a competition between P=O and $N_{pyridine}$ donor sites and the influential factor which determines the winner site is the type of substituents on phosphorus atom.

The C–$N_{(amide)}$ bond length of $\mathbf{C_1}$, in which P=O is the most active donor site, is 1.3719 Å that is about 0.02 Å longer than its similar bond in $\mathbf{C_4}$ with $N_{(pyridine)}$ donor site. A comparison between the crystal structures of $\mathbf{C_4}$ and its related ligand [18] revealed that by coordinating the ligand to Sn, the C–$N_{pyridine}$ bonds get longer (about 0.015 Å) while other bond lengths and angles do not change significantly.

In molecules $\mathbf{C_1}$, $\mathbf{C_3}$ and $\mathbf{C_4}$ the phosphoryl and the carbonyl groups are anti. The phosphorus atoms in these structures have slightly distorted tetrahedral configuration. The bond angles around P(1) atoms in these compounds are in the range of 119.46(6)°–103.67(6)° (in $\mathbf{C_1}$), for the angles O(1)–P(1)–N(3) and N(3)–P(1)–N(1), respectively. In these compounds, the angles OP-N_{amide} (N_{amide} is the nitrogen atom of P(O)N(H)C(O) moiety) are smaller than the angles OPN_{amine} (N_{amine} is the nitrogen atom of P(O)NR moiety) (Table 6). The P=O bond lengths in these complexes are 1.5010(9), 1.4949(13), 1.4810(9) Å that are larger than the normal P=O bond length (1.45 Å) [48]. The C=O bond length in compound $\mathbf{C_4}$ has the highest, 1.2267(15) Å, and in compound $\mathbf{C_3}$, 1.218(2) Å, has the lowest value. The P–N_{amide} bond lengths are longer than the P–N_{amine} bond lengths, because of the resonance interaction of the N_{amide} with the C=O π system that cause a partial multiple bond character in C–N_{amide} (the C–N_{amide} bond lengths are shorter than the C–N_{amine} bond lengths, Table 5). All of these P–N bonds are shorter than the typical P–N single bond length (1.77 Å) [48]. This is likely due to the electrostatic effects (polar bonds) which overlap with P–N σ bond [49]. The environment of all the nitrogen atoms is almost planar (The averages of angles around nitrogens are about 120° and sum of surrounding angles around each of them is near 360°). Similar results were obtained for the nitrogen atoms of other structures that confirm the

Table 6
Selected bond angles (°) for compounds $\mathbf{C_1}$, $\mathbf{C_3}$ and $\mathbf{C_4}$.

$\mathbf{C_1}$		$\mathbf{C_3}$		$\mathbf{C_4}$	
C(1)#1–Sn(1)–C(1)	180.00(6)	C(1)#1–Sn(1)–C(1)	180.00(18)	C(15)#1–Sn(1)–C(15)	180.0
C(1)#1–Sn(1)–O(1)	86.91(5)	C(1)#1–Sn(1)–O(1)	92.08(7)	C(15)#1–Sn(1)–N(4)	89.50(5)
C(1)–Sn(1)–O(1)	93.09(5)	C(1)–Sn(1)–O(1)	87.92(7)	C(15)–Sn(1)–N(4)	90.50(5)
C(1)#1–Sn(1)–O(1)#1	93.09(5)	C(1)#1–Sn(1)–O(1)#1	87.92(7)	C(15)#1–Sn(1)–N(4)#1	90.50(5)
C(1)–Sn(1)–O(1)#1	86.91(5)	C(1)–Sn(1)–O(1)#1	92.08(7)	C(15)–Sn(1)–N(4)#1	89.50(5)
O(1)–Sn(1)–O(1)#1	180.0	O(1)–Sn(1)–O(1)#1	180.00(10)	N(4)–Sn(1)–N(4)#1	180.0
C(1)#1–Sn(1)–Cl(1)	89.61(4)	C(1)#1–Sn(1)–Cl(1)#1	90.80(6)	C(15)#1–Sn(1)–Cl(1)#1	88.90(4)
C(1)–Sn(1)–Cl(1)	90.39(4)	C(1)–Sn(1)–Cl(1)#1	89.20(6)	C(15)–Sn(1)–Cl(1)#1	91.10(4)
O(1)–Sn(1)–Cl(1)	87.62(3)	O(1)–Sn(1)–Cl(1)#1	90.86(3)	N(4)–Sn(1)–Cl(1)#1	89.82(3)
O(1)#1–Sn(1)–Cl(1)	92.38(3)	O(1)#1–Sn(1)–Cl(1)#1	89.14(3)	N(4)#1–Sn(1)–Cl(1)#1	90.18(3)
C(1)#1–Sn(1)–Cl(1)#1	90.39(4)	C(1)#1–Sn(1)–Cl(1)	89.20(6)	C(15)#1–Sn(1)–Cl(1)	91.10(4)
C(1)–Sn(1)–Cl(1)#1	89.61(4)	C(1)–Sn(1)–Cl(1)	90.80(6)	C(15)–Sn(1)–Cl(1)	88.90(4)
O(1)–Sn(1)–Cl(1)#1	92.38(3)	O(1)–Sn(1)–Cl(1)	89.14(3)	N(4)–Sn(1)–Cl(1)	90.18(3)
O(1)#1–Sn(1)–Cl(1)#1	87.62(3)	O(1)#1–Sn(1)–Cl(1)	90.86(3)	N(4)#1–Sn(1)–Cl(1)	89.82(3)
Cl(1)–Sn(1)–Cl(1)#1	180.0	Cl(1)#1–Sn(1)–Cl(1))	180.000(18)	Cl(1)#1–Sn(1)–Cl(1)	180.0
O(1)–P(1)–N(2)	110.58(6)	O(1)–P(1)–N(3)	108.05(8)	O(1)–P(1)–N(2)	116.32(6)
O(1)–P(1)–N(3)	119.46(6)	O(1)–P(1)–N(4)	118.39(8)	O(1)–P(1)–N(3)	114.57(6)
O(1)–P(1)–N(1)	104.44(5)	N(3)–P(1)–N(4)	107.05(8)	O(1)–P(1)–N(1)	105.72(5)
N(2)–P(1)–N(3)	107.12(6)	O(1)–P(1)–N(1)	105.20(7)	N(2)–P(1)–N(3)	105.96(6)
N(2)–P(1)–N(1)	111.29(6)	N(3)–P(1)–N(1)	113.64(8)	N(2)–P(1)–N(1)	106.61(5)
N(3)–P(1)–N(1)	103.67(6)	N(4)–P(1)–N(1)	104.74(8)	N(3)–P(1)–N(1)	107.07(6)
P(1)–O(1)–Sn(1)	141.19(6)	P(1)–O(1)–Sn(1)	151.70(8)		
C(2)–N(1)–P(1)	126.05(9)	C(2)–N(1)–P(1)	124.12(12)	C(1)–N(1)–P(1)	122.76(9)
C(2)–N(1)–H(1)	118.4	C(2)–N(1)–H(1N)	123.0	C(1)–N(1)–H(1N)	116.9
P(1)–N(1)–H(1)	113.3	P(1)–N(1)–H(1N)	112.8	P(1)–N(1)–H(1N)	120.3
C(12)–N(2)–P(1)	126.98(9)	C(8)–N(3)–P(1)	122.45(12)	C(7)–N(2)–P(1)	127.94(9)
C(12)–N(2)–H(2)	115.5	C(8)–N(3)–H(3N)	118.8	C(7)–N(2)–H(2N)	113.0
P(1)–N(2)–H(2)	116.6	P(1)–N(3)–H(3N)	117.1	P(1)–N(2)–H(2N)	116.2
C(8)–N(3)–P(1)	128.38(9)	C(14)–N(4)–P(1)	120.85(12)	C(11)–N(3)–P(1)	126.11(9)
C(8)–N(3)–H(3)	111.8	C(14)–N(4)–H(4N)	117.7	C(11)–N(3)–H(3N)	116.7
P(1)–N(3)–H(3)	114.3	P(1)–N(4)–H(4N)	116.0	P(1)–N(3)–H(3N)	114.6

Table 7
Selected bond lengths (Å) and angles (°) for compound $\mathbf{C_5}$.

$\mathbf{C_5}$			
Sn(1)–C(1)#1	2.126(2)	N(1)–C(2)	1.346(3)
Sn(1)–C(1)	2.126(2)	N(1)–C(6)	1.347(3)
Sn(1)–N(1)	2.3736(17)	N(2)–C(7)	1.340(3)
Sn(1)–N(1)#1	2.3736(17)	N(2)–H(2NB)	0.8406
Sn(1)–Cl(1)#1	2.5799(5)	N(2)–H(2NA)	0.8859
Sn(1)–Cl(1)	2.5799(5)	O(1)–C(7)	1.230(2)
C(1)#1–Sn(1)–C(1)	180.0	N(1)#1–Sn(1)–Cl(1)	89.07(4)
C(1)#1–Sn(1)–N(1)	90.84(7)	Cl(1)#1–Sn(1)–Cl(1)	180.00(2)
C(1)–Sn(1)–N(1)	89.16(7)	C(2)–N(1)–C(6)	118.62(17)
C(1)#1–Sn(1)–N(1)#1	89.16(7)	C(2)–N(1)–Sn(1)	121.39(13)
C(1)–Sn(1)–N(1)#1	90.84(7)	C(6)–N(1)–Sn(1)	119.86(13)
N(1)–Sn(1)–N(1)#1	180.0	C(7)–N(2)–H(2NB)	120.3
C(1)#1–Sn(1)–Cl(1)#1	90.41(6)	C(7)–N(2)–H(2NA)	118.0
C(1)–Sn(1)–Cl(1)#1	89.59(6)	H(2NB)–N(2)–H(2NA)	121.1
N(1)–Sn(1)–Cl(1)#1	89.07(4)	Sn(1)–C(1)–H(1A)	109.5
N(1)#1–Sn(1)–Cl(1)#1	90.93(4)	Sn(1)–C(1)–H(1B)	109.5
C(1)#1–Sn(1)–Cl(1)	89.59(6)	H(1A)–C(1)–H(1B)	109.5
C(1)–Sn(1)–Cl(1)	90.41(6)	Sn(1)–C(1)–H(1C)	109.5
N(1)–Sn(1)–Cl(1)	90.93(4)		

sp^2 hybridization for the N atoms, although due to the repulsion and steric interactions, some angles are greater, and the others are smaller than 120° [50–55].

In the structures of $\mathbf{C_1}$, $\mathbf{C_3}$ intramolecular –Sn–Cl···H–$N_{(amide)}$– and intermolecular $N_{(pyridine)}$···H–$N_{(amine)}$ hydrogen bonds lead to a three dimensional polymeric cluster in the lattice. In the crystalline network of $\mathbf{C_4}$ intermolecular P═O···H–$N_{(amide)}$– hydrogen bonds form centrosymmetric dimmers which beside –Sn–Cl···H–$N_{(amine)}$– intermolecular bonds produce a two dimensional polymeric chain. In $\mathbf{C_5}$ a three dimensional polymeric cluster has been obtained corresponding to the two intermolecular –Sn–Cl···H–$N_{(amide)}$– hydrogen bonds.

4. Conclusions

Some novel organotin complexes of nicotinamide (nia), isonicotinamide (iso) and their phosphoramidate derivatives were synthesized for the first time. Results showed that one of the prepared phosphoramidates connects to Sn(IV) from its $N_{pyridine}$ donor site,

Table 8
Hydrogen bonds for complexes $\mathbf{C_1}$, $\mathbf{C_3}$, $\mathbf{C_4}$ and $\mathbf{C_5}$ (Å and °).

Compound	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
$\mathbf{C_1}$	N(1)–H(1)...Cl(1)	0.92	2.31	3.2161(14)	168
	N(2)–H(2)...O(2)[−*x* + 2,−*y*,−*z* + 2]	0.92	2.05	2.9622(17)	175
	N(3)–H(3)...N(4)[−*x* + 1,−*y*,−*z* + 2]	0.92	2.25	3.1644(19)	174
$\mathbf{C_3}$	N(1)–H(1N)...Cl(1)	0.9000	2.3700	3.2568(16)	166.00
	N(3)–H(3N)...O(2) [−*x*,−*y* − 1,−*z* + 1]	0.8300	2.2200	3.028(2)	165.00
	N(4)–H(4N)...N(2) [−*x*,−*y*,−*z* + 1]	0.7800	2.3600	3.129(2)	168.00
$\mathbf{C_4}$	N(1)–H(1N)...O(1)[−*x* + 2,−*y* + 1,−*z* + 2]	0.90	1.92	2.8005(13)	166
	N(2)–H(2N)...Cl(1)[−*x* + 1,−*y* + 2,−*z* + 2]	0.90	2.60	3.4844(11)	166
	N(3)–H(3N)...O(2)	0.90	2.54	3.4844(11)	118
$\mathbf{C_5}$	N(2)–H(2NB)...Cl(1)[*x*,−*y* + 3/2,*z* + 1/2]	0.84	2.58	3.395(2)	165
	N(2)–H(2NA)...Cl(1)[−*x*−1,*y* + 1/2,−*z* − 1/2]	0.89	2.49	3.336(2)	159

just like nia and iso, while others act as P=O donor ligands. It seems that in these complexes there is a competition between P=O and $N_{pyridine}$ donor sites and the influential factor which determines the winner site is the type of substituents on phosphorus atom. According to the crystal structures, determined for some of the synthesized complexes, –Sn–Cl···H–N– major hydrogen bonds beside other electrostatic interactions produced a two dimensional polymeric chain in one of the complexes' crystalline lattice and a three dimensional polymeric cluster in others.

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Appendix A. Supplementary material

CCDC 727895, 740181, 740182 and 727889 contain the supplementary crystallographic data for the structures **C_1**, **C_3**, **C_4** and **C_5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.02.004.

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